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The TMS 2011 Annual Meeting Supplemental Proceedings, Volume 2: Materials Fabrication, Properties, Characterization, and Modeling, is a collection of papers from the 2011 TMS Annual Meeting and Exhibition, held February 27-March 3, in San Diego, California, U.S.A. The papers in this volume were selected based on technical topic compatibility and represent thirteen symposia from the meeting. This volume, along with the other proceedings volumes published for the meeting, and archival journals, such as Metallurgical and Materials Transactions and the Journal of Electronic Materials, represents the available written record of the 74 symposia held at the 2011 TMS Annual Meeting.

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FABRICATION OF GOLD-PLATINUM NANOALLOY BY HIGH-INTENSITY LASER IRRADIATION OF SOLUTION

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Keywords: Femtosecond laser, Liquid, Au-Pt nanoalloy

Abstract
Gold-platinum (Au-Pt) solid solution nanoalloys were fabricated by high-intensity femtosecond laser irradiation of mixed solution of auric and platinum ions. Photo-absorption spectra of prepared solutions were measured by UV-visible spectrophotometer before and after irradiation. The fabricated particles were characterized by TEM and XRD. While two representative diffraction peaks are commonly observed between peak the positions of pure bulk gold and platinum for bulk because of a large immiscibility gap in a Au-Pt binary system, only a single diffraction peak was detected for single-nanometer sized Au-Pt nanoalloy particles fabricated by high-intensity laser irradiation of mixed solution of auric and platinum ions with the concentration of $5.0 \times 10^{-4}$ M. This finding demonstrates that solid solution Au-Pt nanoalloys are successfully fabricated only by high-intensity laser irradiation of aqueous solution without any chemicals.

Introduction
Binary alloy nanoparticles (NPs) have been intensively studied especially in the research field of catalysis\(^1,2\) because of their bifunctional catalytic properties. Currently, gold-platinum (Au-Pt) nanoalloys are attracted much attention for electrocatalysis in a fuel cell\(^3,4\). The Au-Pt nanoalloys are expected to provide synergistic catalytic activities such as suppression of adsorbed poisonous species like carbon monoxide (CO) on Pt atoms, and the change in electronic band structure to modify the strength of the surface adsorption. The decreases of activation energy promoting oxidative desorption and suppressing the adsorption of CO was considered as a factor that leads to a sufficiently high adsorptivity to support catalytic oxidation in alkaline electrolytes\(^5,6\). Au-Pt nanoalloys are prepared mainly by chemical processes\(^7-13\) in a form supported on a specially prepared substrate such as SiO\(_2\)\(^14\) and carbon\(^12,13\) to date. The process commonly needs a series of complex procedures and often uses some chemicals that might be highly reactive and cause environmental and biological problems.

Recently, we have demonstrated a method for the preparation of metal NPs of gold\(^14\), platinum\(^15\) and silver by using high intensity laser irradiation of the metal ion solution. This technique is expected to produce many kinds of metal and their alloy NPs directly in the solution without any complex procedures and harmful chemicals. In this study, we describe the fabrication of Au-Pt nanoalloy in a mixed solution of auric and platinum ions by high intensity laser irradiation of the solution. Effects of the fraction of auric and platinum ions in the solution on the composition and structure of Au-Pt nanoalloys were investigated. The fabrication mechanism of the NPs was also discussed.

Experimental
Mixed solutions of auric and platinum ions with different fraction were prepared by the following procedure. Auric and platinum aqueous solutions were separately prepared by dissolving hydrogen tetrachloroaauric (III) tetrahydrate powder (HAuCl₄·3H₂O, Wako Pure Chemical Industries, Ltd., > 99.9 %) and hydrogen hexachloroplatinic (IV) hexahydrate powder (H₂PtCl₆·6H₂O, Sigma-Aldrich Co., > 99.9 %) in extra-pure water. The concentration of each solution was set to 5.0×10⁻⁴ M. Subsequently, both solutions were mixed with different molar fractions. Samples are labeled by the molar fraction of auric and platinum ions. For example, 50 % of auric and platinum solution is labeled as Au50Pt50. All the solutions were transparent, and no apparent difference was observed. Figure 1(a) shows UV-visible absorption spectra of prepared solutions with different molar fraction of auric and platinum ions measured by a UV-visible spectrophotometer (JASCO Co., V630 iRM). UV-visible absorption spectrum was shifted from that of auric (Au00Pt00) to platinum solution (Au00Pt100) with decreasing the fraction of auric ion in the solution. As a target of laser irradiation, 3 milliliters of each aqueous solution was dispensed in a 10×10×45 mm quartz glass cuvette that is optically transparent at the wavelength of incident laser light. Femtosecond laser beam was generated from a chirped-pulse amplified Ti:sapphire laser system with the wavelength of 800 nm. The pulse energy was 5 mJ with the pulse width of 100 fs and the repetition rate was 30 Hz. The laser beam was introduced to the cuvette normal to its surface and tightly focused in the solution by an aspheric lens with the focal length of 8 mm and the numerical aperture of 0.5. The spot diameter was estimated to be 175 μm in a diameter. Theoretical estimation of the laser intensity was 2.1×10¹⁴ W/cm² taking into account that a laser beam radius is 3.2 mm before the focusing lens, and the refractive index of the solution is 1.33 (water). The irradiation time was set to 30 min in every experiment. Optical characteristics of the solution after laser irradiation were evaluated by a UV-visible spectrometer. Transmission electron microscopes (TEM: JEOL, JEM2000EXII) were employed to take electron micrographs of the products after irradiation. The samples for TEM observation were prepared by falling a few drops of the solution on a carbon-coated copper grid (Okenshioji Co., Ltd., Micro grid type-B) immediately after the irradiation and dried in air at room temperature. The samples for the XRD measurement were prepared by freeze-drying and placing the obtained powder on a non-reflecting single crystal silicon plate (Rigaku Co.), which is specially made to avoid any diffraction peak of silicon over measurement range.

Figure 1. Uv-vis. absorption spectra of the mixed solution of auric and platinum ions with different fractionsf (a) before and (b) after irradiation.
Results

A tiny flash of luminescence and fine bubbles were observed around the focal point during laser irradiation. These gases were identified as oxygen and hydrogen by chromatographic analysis (GC-8A, Shimadzu Co.). The gases were probably produced by the decomposition of water molecules through the laser induced break down facilitated by a high intensity laser field. The transparency of the solution gradually changed during the laser irradiation and resultant color of the solution after 30 minutes irradiation strongly depended on the molar fraction of auric and platinum ions in the solution; red-purple for Au100Pt0 and light-brown for Au0Pt100.

Figure 1(b) shows a representative set of UV-visible absorption spectra of the solutions with different molar fractions after irradiation. The spectra were measured promptly after the irradiation. In the spectrum of auric solution (Au100Pt0), an absorption peak at 520 nm was observed arising from surface plasmon resonance (SPR) of gold nanoparticles. The peak position shifted to shorter wavelength, and the absorbance decreased with the decrease in the fraction of auric ion in the solution.

TEM bright field images of the particles are shown in Fig. 2. Mean particle size of each sample evaluated from the TEM images was also shown below the micrograph. As seen in the figure, particle size in the micrographs became smaller with the decrease in the fraction of auric ion in the solutions. This result is comparable to the fact that gold particles tend to grow and crystallize faster than other noble metals such as palladium and platinum because of its property of low melting point (1336 K) and no affinity to oxygen.

![Figure 2. TEM images of the NPs fabricated by high intensity laser irradiation of mixed solution of auric and platinum ions with different fractions.](image-url)
To determine the structural characteristics of the fabricated particles, XRD measurement were employed for all samples. A representative set of profiles is shown in Fig. 3. The typical XRD peak positions of gold and platinum from 1 1 1 planes are also indicated by broken lines for comparison. As seen in the figure, the diffraction patterns of the particles in Au100Pt0 and Au0Pt100 are indexed to be an fcc-type cubic lattice of bulk gold and platinum. XRD peaks in the profile were shifted from the peak position of gold to that of platinum with decreasing the fraction of auric ion in the solution. The results from the structural analysis of the fabricated particles by using Integrated X-ray Powder Diffraction Software (Rigaku Co.) are summarized in Table 1. Crystalline sizes of the particles calculated by Scherrer’s equation seemed to be larger than the particle sizes observed in TEM images (Fig. 2). This might be arising from crystal growth during sample preparation by freeze-drying. The crystalline sizes varied from 50 nm to 6 nm with the decrease in the composition of auric ion in the solution. This result denotes the same tendency as the result from TEM observation (Fig. 2). Lattice constants of the particles fabricated in the solutions of Au100Pt0 (a = 4.082 Å) and Au0Pt100 (a = 3.927 Å) were in a good agreement with those of bulk gold and platinum. Interestingly, lattice constant of the fabricated nanoalloy was almost linearly changed from that of bulk gold to platinum depending on the fraction of auric and platinum ions in the mixed solutions. This result clearly indicates the solid solution Au-Pt nanoalloys with intended composition were successfully fabricated in the solutions only by high-intensity laser irradiation of solutions without any chemical.

Figure 3. XRD profiles of the NPs fabricated by high intensity laser irradiation of mixed solution of auric and platinum ions with different fraction.

Table 1. Characteristic parameters of nanoparticles evaluated from XRD peaks

<table>
<thead>
<tr>
<th>Solution</th>
<th>2Θ (deg)</th>
<th>d (Å)</th>
<th>Peak (cps)</th>
<th>FWHM (deg)</th>
<th>a (Å)</th>
<th>SizeXRD (Å)</th>
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<tbody>
<tr>
<td>Au100Pt0</td>
<td>38.157</td>
<td>2.357</td>
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<td>0.174</td>
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<td>0.589</td>
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<td>1.259</td>
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<td>1.428</td>
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